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(56) Documents Cited

GB 1333275 A

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(58) Field of Search

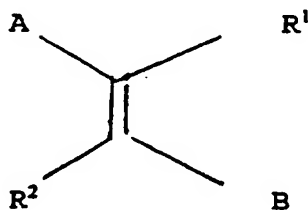
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(54) Polymeric material

(57) A method of preparing a polymeric compound which comprises providing a compound of general formula



or a salt thereof where A and B are the same or different and at least one comprises a relatively polar atom or group and R¹ and R² independently comprise relatively non-polar atoms or groups, in a solvent of a type in which ethene itself is generally insoluble and causing the groups C=C in said compound to react with one another to form a polymeric structure. The polymeric compound may be reacted with a second compound, for example polyvinylalcohol, collagen or the like to produce a colloid or gel which may have applications in the treatment or burns or recovery of oils.

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FIG. 2.

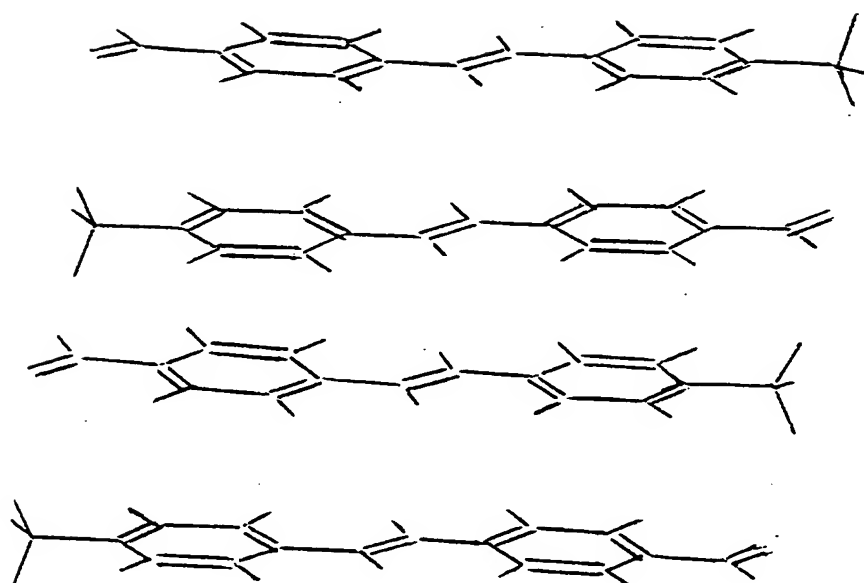
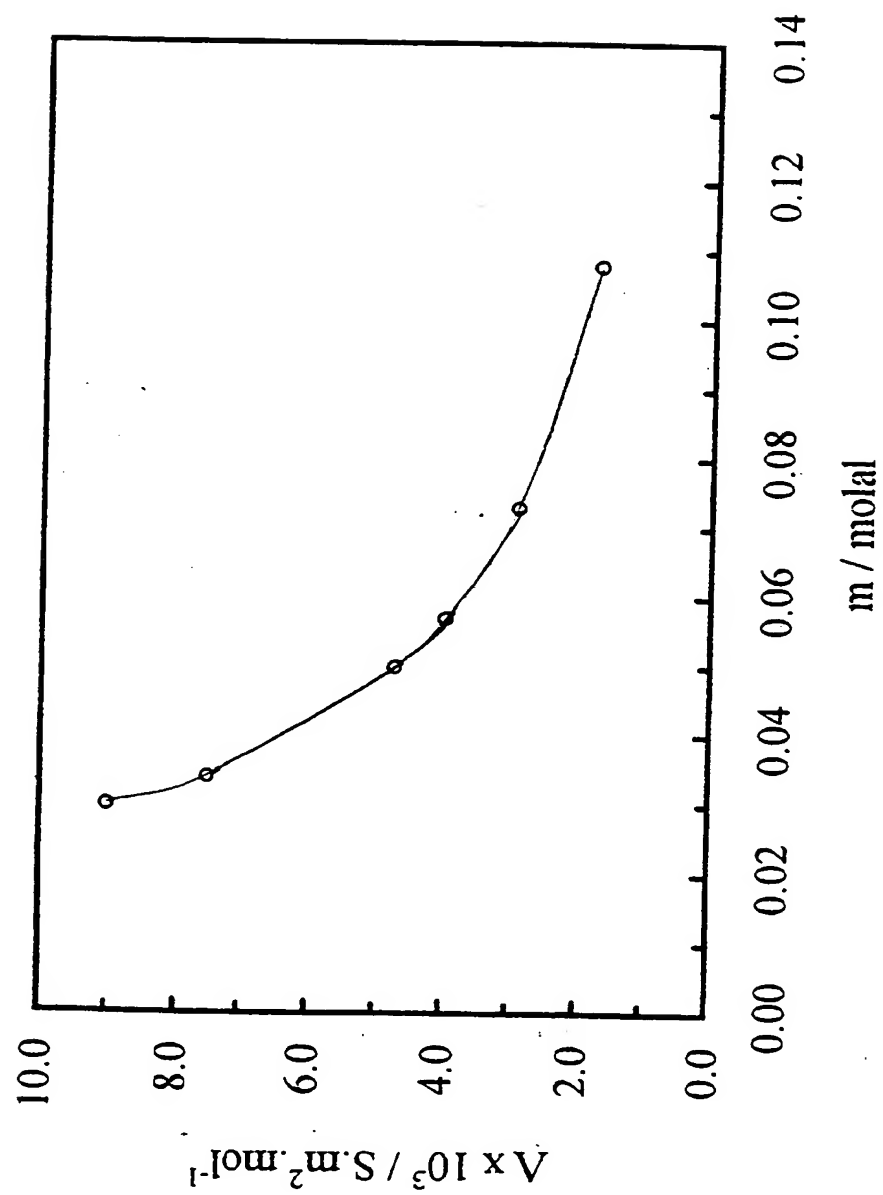
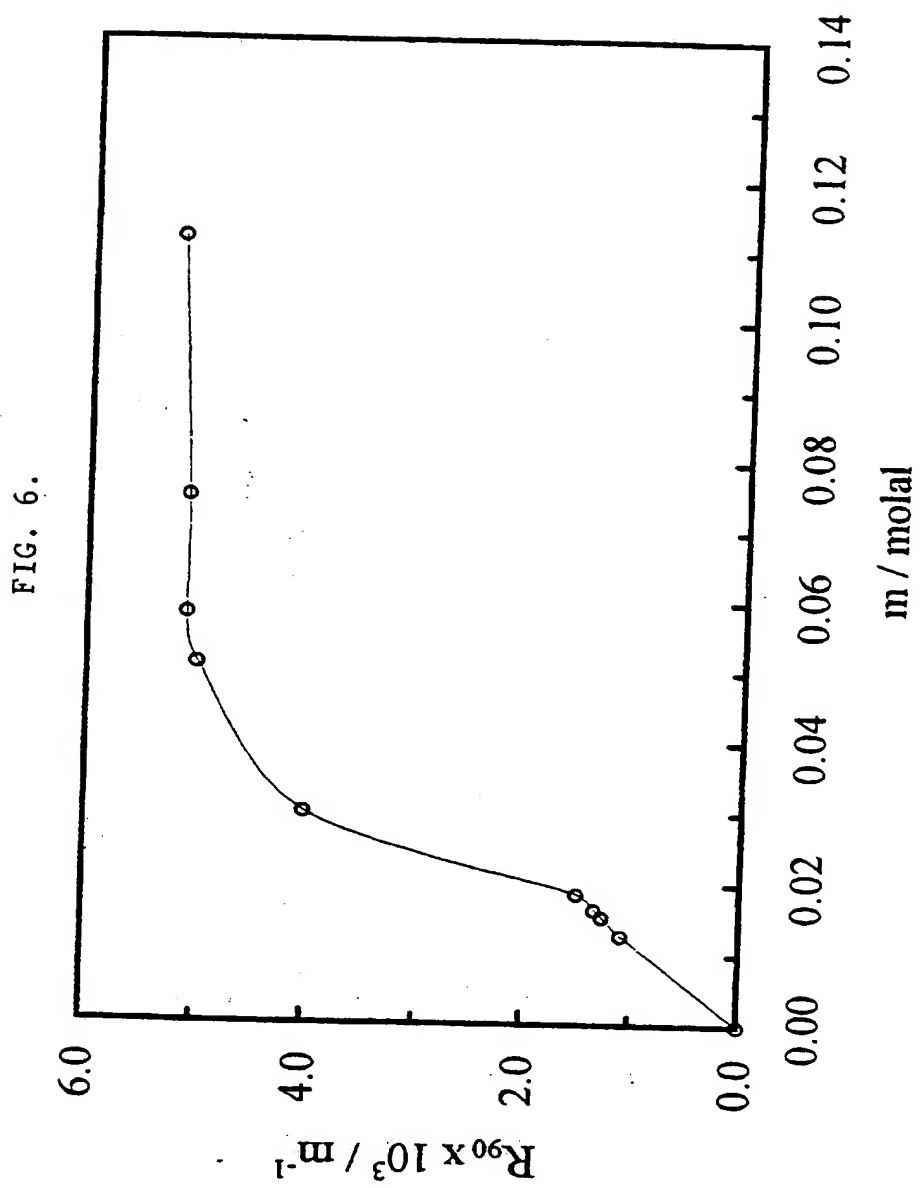


FIG. 4.





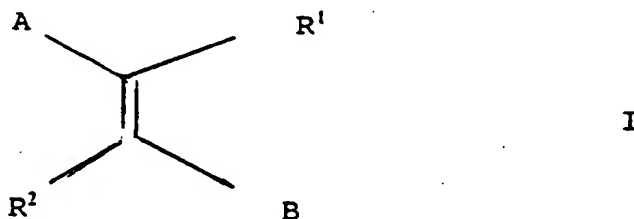
POLYMERIC MATERIAL

This invention relates to a polymeric material and particularly, although not exclusively, relates to a polymeric material which is at least partially formed from a 1,2-substituted ethene compound, for example a substituted styrylpyridinium compound.

UK Patent No. GB 2 030 575 B (Agency of Science and Technology) describes a photosensitive resin which is prepared by reacting a styryl pyridinium salt which possesses a formyl or acetal group on the styryl phenyl group with a polyvinyl alcohol or a partially saponified polyvinyl acetate. In the resin, the group $-\text{CH}=\text{CH}-$ is photosensitive and, accordingly, the resin can be used in, for example, screen printing where it is found to exhibit high sensitivity.

The present invention is based on the discovery of surprising properties of 1,2-substituted ethene compounds of the type described which allow polymeric materials to be prepared which have various useful properties.

According to a first aspect of the present invention, there is provided a method of preparing a first polymeric compound which comprises providing a compound of general formula



Said compound of general formula I may be provided in said solvent at a concentration of at least 0.5 wt%, preferably at least 1.0 wt% and, more preferably, at least 1.5 wt%.

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The groups C=C in said compound are preferably caused to react in a photochemical reaction. Preferably, the method comprises inducing a photochemical reaction, suitably using ultraviolet light. Preferably, in the method, light of up to 500 nm wavelength is used.

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Preferably, A and B are independently selected from optionally-substituted alkyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aromatic and heteroaromatic groups. Where group A or B has a cyclic structure, five or, more preferably, six membered rings are preferred.

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More preferably, A and B are independently selected from optionally substituted aromatic and heteroaromatic groups, with five or, more preferably, six-membered such groups being especially preferred. Preferred heteroatoms of said heteroaromatic groups include nitrogen, oxygen and sulphur atoms of which oxygen and especially nitrogen, are preferred. Preferred heteroaromatic groups include only one heteroatom. Preferably, a or said heteroatom is positioned furthest away from the position of attachment of the heteroaromatic group to the group C=C. For example, where the heteroaromatic group comprises a six-membered ring, the heteroatom is preferably provided at the 4-position relative to the position of the bond of the ring with the group C=C.

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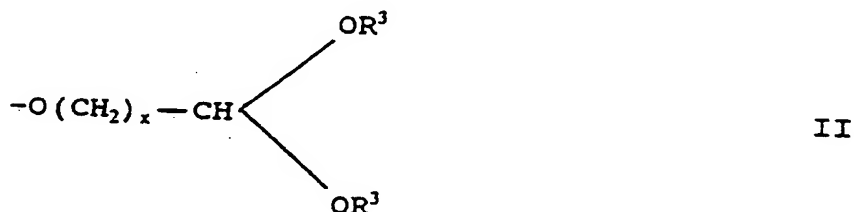
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Unless otherwise stated, optionally substituted groups described herein, for example groups A and B, may be substituted by halogen atoms, and optionally

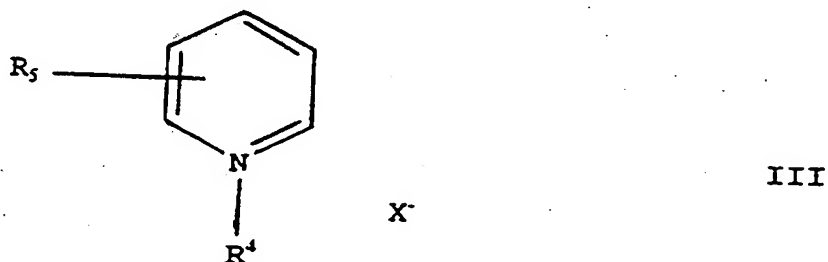
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Preferably, group A represents a phenyl group substituted, preferably at the 4-position relative to the group C=C, by a formyl group or a group of general formula



where x is an integer from 1 to 6 and each R₃ is independently an alkyl or phenyl group or together form an alkalene group.

15 Preferably, group B represents a group of general formula



wherein R⁴ represents a hydrogen atom or an alkyl or aralkyl group, R⁵ represents a hydrogen atom or an alkyl group and X⁻ represents a strongly acidic ion.

30 Preferred compounds of general formula I for use according to the present invention include those referred to on page 3 line 8 to line 39 of GB 2 030 575 B and said compounds are hereby incorporated into this specification.

example an ester, and an amine group. Preferred second polymeric compounds include optionally substituted, preferably unsubstituted, polyvinylalcohol, polyvinylacetate, polyalkylene glycols, for example
5 polypropylene glycol, and collagen (and any component thereof).

Preferably, said second polymeric compound is a solid under ambient conditions. Preferably, said intimate mixing
10 is carried out at an elevated temperature. Preferably, mixing is carried out in the same solvent in which compound I is prepared. The mixture may include further polymeric compounds which may be the same type as said second polymeric compounds described above.

15 The ratio of the wt% of said first polymeric compound to the wt% of said second polymeric compound (or the sum of the wt% of the second compound and any further compounds) in the mixture is found to influence
20 significantly the properties of the formulation prepared. The ratio of the wt% of said first polymeric compound to that of said second polymeric compound may be in the range 0.01 to 100, is preferably in the range 0.05 to 50 and more preferably in the range 0.3 to 20.

25 Preferably, water is removed from said formulation to produce a solid material, for example in the form of a film.

30 According to a fourth aspect of the present invention, there is provided a formulation comprising a first polymeric compound according to said first or second aspects and a second polymeric compound as described in said third aspect.

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ingredients and since it is understood that preparations prepared as described herein are biocompatible, the sheet materials may be used in burns treatment.

5 It has been noted that if oil (or the like) is contacted with the reaction mixture of said fifth aspect, up to 50 wt% of oil can be emulsified by the mixture and that the resultant gel holds the oil in a solid matrix. Accordingly, in a sixth aspect, the invention provides a
10 method of collecting and/or isolating and/or emulsifying oil (or the like) which comprises contacting oil (or the like) with a reaction mixture according to said fifth aspect so that said oil (or the like) becomes incorporated into a material, for example a gel which is formed.

15 The invention extends to a colloid or gel preparable by the method of the fifth aspect.

 According to a seventh aspect, there is provided a
20 novel third polymeric material which comprises the reaction product of a compound of general formula IV with a second polymeric material as described herein.

 Any feature of any aspect of any invention or example
25 described herein may be combined with any feature of any aspect of any other invention or example described herein.

 Specific embodiments of the invention will now be described, by way of example, with reference to the
30 accompanying figures, wherein:

 Figure 1 is a graph showing vapour pressure measurements on aqueous solutions of 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphonate
35 (SbQ) at 37°C as a function of concentration;

- ii. Vapour pressure measurements - made using a Knauer vapour pressure osometer standardised against Analar NaCl solutions.
- 5 iii. An analysis of the energy of the structure of the SbQ molecule, minimised in water - made using a Hyperchem (Trade Mark) molecular modelling package based on MM⁺ force field calculations
- 10 iv. Conductivity measurements - made using a Wayne Kerr model B905 automatic measurement bridge.
- 15 v. Density measurements - made as described in Eur. Polym.J., 1987, 23, 711 in order to provide apparent molar volume values.
- 20 vi. Light scattering measurements - made using a Sofica photogoniometer model 42000 modified to use a Uniphase 1mW HeNe laser, operating at 543 nm.
- vii. Heats of dilution measurements - made using a LKB Flow Microcalorimeter model 2107-121/127.

Results

25 Referring to Figure 1, the ratio $\Delta t/C$ represents the difference in temperature between the solvent reference probe and the solution probe at a concentration C in g/kg. The plot shows two linear regions, both with good correlation coefficients of 0.996 and 0.998 respectively, intersecting at a concentration value of 1.25% w/w. The intercept of the low range of solution concentrations was utilised in the usual manner to yield a value for the number average molar mass for SbQ of 341, close to the expected value of 335. The difference of slope at the

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form above this concentration, exactly what might be expected to happen when aggregating to form a micelle.

Referring to Figure 6, the sharp increase in scattering which occurs at concentrations approaching 0.04M indicates the appearance of larger particles i.e. micelles.

Referring to Figure 7, the heats of dilution measurements also show a sharp change of slope, in this case at 0.035M, yet again indicating a major change in the solution state of the solute, from monomer to micelle has occurred.

It should be appreciated from the above that the close correlation between the concentration dependence behaviour of all the experimental measurements is good confirmation of the existence of a monomer-micelle equilibrium in the aqueous solutions of SbQ. This behaviour is utilised in the following examples.

Example 1

Preparation of poly(1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene(Compound II shown below)

An aqueous solution of greater than 1 wt% SbQ was exposed to ultraviolet light. This results in a photochemical reaction between the carbon-carbon double bonds of adjacent 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphate molecules (I) in the aggregate, producing a polymer, poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene (II), as shown in the reaction scheme below. It should be

slowly with constant stirring to disperse the powder. Final dissolution was achieved by maintaining the solution at a temperature of 60°C for a period of 6 hours. The resultant poly(vinyl alcohol)/poly(1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene) solution may be cast as a film on PTFE sheet and dried under vacuum. The solid blend is light stable and can be stored in a desiccator until required.

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Example 3

Preparation of gel

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The film described in Example 2 may be re-dissolved in water together with an acid, for example paratoluene sulphuric acid. This causes an acid catalysed aldol condensation reaction according to the scheme below.

gelling time is dependent on the concentration of acid used. 0.1 wt% acid gives a gelling time of 16 hours, whereas 1 wt% acid gives a gelling time of 10 minutes.

5 Properties of gels prepared following general
 procedures described herein

- 10 1. Gels formed using 2.5 to 13 wt% poly(vinyl alcohol) do not melt or show any visual sign of phase changes on heating to 100°C; at higher temperatures the gel "chars" but does not burn.
2. The gels are rigid and optically clear.
- 15 3. The time required for gelation can be controlled by varying the concentration of acid used to catalyse the gelling reaction. The variable gel time permits the casting of different shapes of gel merely by pouring the reaction mixture into a mould. There is
20 no significant shrinkage of the material on gel formation.
4. The gels are insoluble in all common organic
25 solvents, although some gels swell slightly. The gels are also insoluble in aqueous solutions.
5. Rigid gels can be produced using a mixture of 50 wt% collagen and 50 wt% poly(vinyl alcohol) instead of
30 only poly(vinyl alcohol) described in Examples 2 and 3. The gels produced show resistance to organic solvents and limited swelling in water.
6. After addition of the acid to catalyse the gelling reaction in Example 3, up to 50 wt% oil may be

5 All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

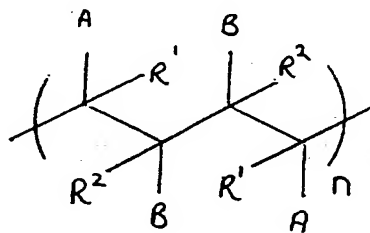
10 Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

15 The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

6. A method according to any preceding claim, wherein A and B are independently selected from optionally-substituted alkyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aromatic and heteroaromatic groups.

7. A method according to any preceding claim, wherein A and B each independently represent optionally-substituted aromatic or heteroaromatic groups.

8. A novel first polymeric compound having the formula



wherein A and B are the same or different and at least one comprises a relatively polar atom or group, R¹ and R² independently comprise relatively non-polar atoms or groups and n is an integer.

9. A method of preparing a formulation comprising providing a first polymeric compound prepared in a method according to any of claims 1 to 7 or according to claim 8 in a solvent together with a second polymeric compound and intimately mixing the compounds.

10. A method according to claim 9, wherein said second polymeric compound includes one or more functional groups capable of reacting with said first polymeric compound.

11. A method according to claim 9 or claim 10, wherein said second polymeric compound is selected from optionally substituted polyvinylalcohol, polyvinylacetate,



Application No: GB 9719759.4
Claims searched: 1-7

Examiner: Alan Kerry
Date of search: 27 January 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C3P PKH; PDM

Int Cl (Ed.6): C08F 2/10, 12/22, 20/06, 26/06, 112/14, 126/06

Other: Online database: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB1333275 A (DOW) - see Claim 1 and the Examples	1-3
X	US 5258473 (NIESSNER) - see Claim 1 and Example 1	1-3
X	US 4709767 (ALEXANDER) - see Example 2	1-3
X	US 4039542 (PANZER) - see Example 33	1-3

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.